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EQUILIBRIUM OF OXIDATION-REDUCTION CONVERSION OF GRANULATED REDOXITES

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Abstract

A thermodynamic calculation is made of the degree of equilibrium oxidation-reduction conversion of quinone-hydroquinone and metal-containing redoxites; its experimental verification with respect to the redox potentialwas carried out. The effect of various factors on the completeness of the utilization of the theoretical potential is noted.

The investigation of the equilibrium of the oxidation-reduction conversion of redoxites is based on measuring potentials and the redox potential. In addition to determining the potentials [1], it is important to establish the thermodynamic possibility and the completeness of this conversion and to compare these characteristics with experimental data. This study presents a theoretical calculation of the standard free energy ΔG^0 of oxidation-reduction reactions involving redoxites and the degree of conversion F of the latter; also examined are the experimental results of measuring the redox potential of several resins of practical value.

Use was made of the EO-7 quinone-hydroquinone electron exchanger and the metallized EI-5, EI-5u, EI-12, EI-15, and EI-21 electron ion-exchangers with copper and bismuth groups [2] dispersed in the pores of the cation exchangers. To determine the redox potential, resins reduced in advance with an alkaline solution of sodium hydrosulfite and converted to the hydrogen form were brought into reaction with an oxidizer dissolved in water or in 1 N H_2SO_4, following the technique given in [3,4]. An analysis of the structural changes of the resin upon oxidation was made with IR absorption spectra taken with an IKS-14A spectrophotometer.

First let us dwell on a description of the equilibrium state of a system of a dissolved linear redoxite with quinone-hydroquinone groups and a series of oxidizers forming a homogeneous phase with the polymer. The values of the free energy ΔG^0 of the reaction and the difference $\Delta\phi^0$ of the equilibrium potentials of the interacting redox couples in standard conditions, calculated from the data in [5], are presented in Table 1.

The degree of conversion of the redoxite takes on a limiting value already when $\Delta\phi^0 \approx 0.1$ V, thus indicating complete irreversibility of the reaction. An exception is the ferro-ferri couple; when in contact with an equivalent amount of this couple, the redoxite is capable of being oxidized only by 90 percent due to the insufficiently high potential difference. For relatively weak oxidizers of the ferro-ion type, finding the ratio α of the starting amounts of oxidizer and redoxite for which F would reach a specified value is possible based on the equation

$$(1+k^{-1})\alpha f^2-(2\alpha+1)f+(2+\alpha)f-1=0 \qquad (1)$$

presented in [1], with reference to $F = \alpha f$. According to (1), for F to reach 99.9 percent, α must be 3.23, that is, complete oxidation of the redoxite requires a more than threefold excess of ions of trivalent iron compared with the amount of the reduced form of the resin that is used.

TABLE

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Oxidation-reduction couple	ΔG^0, kcal/mole	$\Delta\varphi^0$, V	F	Oxidation-reduction couple	ΔG^0, kcal/mole	$\Delta\varphi^0$, V	F
Fe^{3+}/Fe^{2+}	—3,7	0,082	0,9	H_2O_2/H_2O	—49,6	1,071	1,0
VO_2^+/VO^{2+}	—13,7	0,301	1,0	$S_2O_8^{2-}/SO_4^{2-}$	—60,5	1,571	1,0
Cl_2/Cl^-	—31,5	0,661	1,0	$Cr_2O_7^{2-}/Cr^{3+}$	—91,5	0,961	1,0
Ce^{4+}/Ce^{3+}	—37,9	0,911	1,0	MnO_4^-/Mn^{2+}	—190,0	0,521	1,0
O_2/H_2O	—49,0	0,531	1,0				

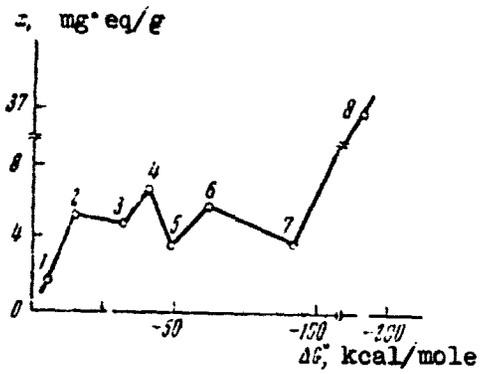

Fig. 1. Amount x of oxidizer -- reduced by EO-7 redoxite -- consisting of 0.001 N solutions prepared on the basis of 1 N H_2SO_4, as a function of the standard free energy ΔG^0 of the reaction. Oxidizers: 1. Fe^{3+} 2. VO_2^+ 3. Cl_2 4. $[Ce(SO_4)_3]^{2-}$ 5. H_2O_2 6. $S_2O_8^{2-}$ 7. $Cr_2O_7^{2-}$ and 8. MnO_4^-

The solid redoxite with quinone-hydroquinone groups has the same ΔG^0 as the dissolved redoxite. The difference is that the activities of the solid phases are equal to unity and the equilibrium position depends only on the activity ratio of the dissolved constituents.

Therefore the principal thermodynamic quantity describing the reactivity of the redoxite is the free energy ΔG^0, which can also be expressed electrically, by here assigning a formal significance to the equilibrium potential of the redoxite. From Table 1 it follows that all the oxidizers used virtually completely oxidize the quinone-hydroquinone redoxite EO-7 and its redox potential should not depend on the nature and concentration of the oxidizer.

Actually, experimental data from a study of the equilibrium state of the EO-7 electron exchanger in the presence of different oxidizers (Fe^{3+}, VO_3^+, O_2, Cl_2, H_2O_2, $[Ce(SO_4)_3]^{2-}$, $S_2O_8^{2-}$, $Cr_2O_7^{2-}$, and MnO_4^-) show that in 0.001 N solutions the redox potential with respect to ions of trivalent iron and oxygen remain constant, 1.6-1.9 mg·eq per g of air-dried resin. With rise in concentration

by three orders, the amount of reduced iron ions rises somewhat (by 1.5 times). According to spectroscopic investigations, this fact must be attributed to the irreversible oxidation of the matrix.

As for all the remaining oxidizers, the reducing ability of the electron exchangers is dependent on the nature of the reagent, although it would appear that the redox potential should be determined only by the number of hydroquinone groups. And the experimental values of the amount of absorbed oxidizer x do not correlate with the standard change in free energy ΔG^0, which is shown by Fig. 1. With rise in the oxidizer concentration in solution, the consumption of reagent increases, accompanied by the simultaneous weight loss of the polymer, amounting in some cases to 100 percent, as can be seen from Fig. 2. The consumption of oxidizers that is supra-equivalent compared with the electron exchange capacity indicates the participation in the oxidation-reduction process of both hydroquinone groups and the polymer matrix, subjected to irreversible oxidation. Prolonged action of even dilute oxidizer solutions causes significant changes in the IR absorption spectrum of the EO-7 redoxite. The intensity of the band of the valency oscillations of the hydroxyl groups (ν = 1350 cm^{-1}), caused by the formation of quinone groups, decreases. The most complete conversion occurs under the effect of oxygen and ferro-ions. Simultaneously, in the region of the valency oscillations of the C=O groups of the carboxylic acids additional absorption bands appear (ν = 1706 and 1695 cm^{-1}) uncharacteristic of the polymer; and substantial changes in the spectrum of the resin caused by the state of the $-CH_2-$ groups (ν = = 1430 cm^{-1}) are observed. The absorption intensities in the region of the valency oscillations of the -OH, C=O, and $-CH_2-$ groups, calculated by the base line method, are shown in Fig. 3. Dashed lines I and II characterize the behavior of the redoxite in a 1 N aerated H_2SO_4 solution. The rise in the intensity of

absorption of the carboxyl groups and the decrease in the intensity of the methylene groups suggest that rupture occurred in the methylene bridges between the phenol and the quinone rings and that carboxylic acids were formed. Some oxidizers are capable of rupturing the benzene ring by oxidizing it to unsaturated acids.

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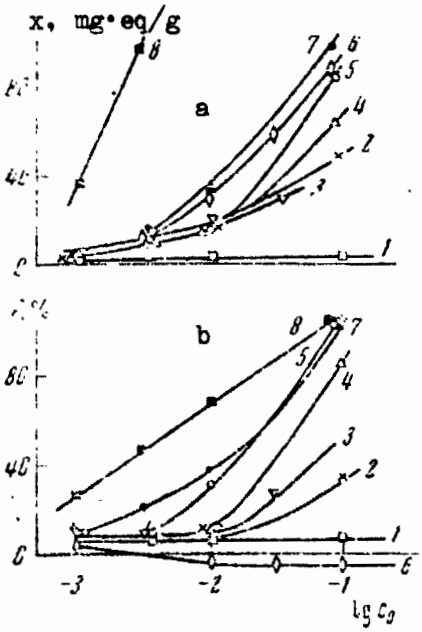

Fig. 2. Amount x of reduced oxidizer (a) and change in weight P of EO-7 redoxite (b) as a function of concentration of oxidizer in 1 N H_2SO_4. Oxidizers: 1. Fe^{3+} 2. VO_2^+ 3. H_2O_2 4. $S_2O_8^{2-}$ 5. $Cr_2O_7^{2-}$ 6. Cl_2 7. $[Ce(SO_4)_3]^{2-}$ and 8. MnO_4^-

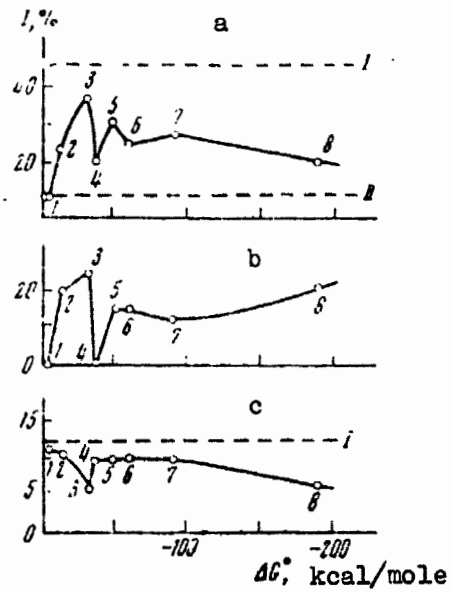

Fig. 3. Absorption intensity J of bands: a. hydroxyl b. carboxyl, and c. methylene groups in spectrum of redoxite treated with solutions of oxidizers: 1. Fe^{3+} 2. VO_2^+ 3. Cl_2 4. $[Ce(SO_4)_3]^{2-}$ 5. H_2O_2 6. $S_2O_8^{2-}$ 7. $Cr_2O_7^{2-}$ and 8. MnO_4^-. I and II. intensity of group 'n redoxite reduced and oxidized by oxygen, respectively

For copper- and bismuth-containing resins EI-5, EI-5u, EI-15, and EI-21, the considerable difference in the standard potentials of the metal and the conversion product of the metal when in contact with oxygen ($\sim$ 0.6-0.9 V) corresponds to the virtually complete oxidation of the redoxites, where the value of F reaches its maximum. Table 2 gives the redox potential of the redoxites studied, found with respect to oxygen and the number of metal groups. The values of the equilibrium redox potential in many cases do not agree with the absorptivity calculated from the total amount of the metal per unit redoxite volume. It is not all the metal dispersed in the pores of the cation exchanger that enters into reaction, but generally those atomic layers that are most accessible to the oxidizer. It is also possible that a relative decrease in the amount of copper reacting with the oxygen with increase in its total content is observed, for example, in going from EI-5 to EI-5u. For EI-12 this difference is most clearly defined, since the access of the oxidizer to the copper groups is hindered by the quite rigid structure of the matrix. At the same time, macroporous redoxite EI-51 has closer potential values found by the two methods described. /642

TABLE 2

Redoxite type	Nature of matrix	Redoxite group	F, mg·eq/ml for O_2	F, mg·eq/ml for metal	Redoxite type	Nature of matrix	Redoxite group	F, mg·eq/ml for O_2	F, mg·eq/ml for metal
EI-5	KU-11	Copper	2.0	2.0—2.5	EU-21	KU-23	Copper	10.3	12.5
EI-5u	"	"	3.9	5.0—5.6	EU-15	KU-11	"	3.1	3.8—4.0
EI-12	KU-1	"	2.0	5.6					

Thus, steric hindrances caused by the necessity of the oxidizer to diffuse into the solid porous phase do not permit the full utilization of the theoretical potential; thus, when determining the reducing ability of a redoxite, one must consider the potential with respect to each specific oxidizer that is nondestructive.

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